

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

N.D.

SPECIFICATION NO. 777,679

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Permachem Corporation, a corporation organised under the laws of the State of Florida, United States of America, of 5610 Georgia Avenue, West Palm Beach, Florida, United States of America.

I THE PATENT OFFICE,
1st July, 1957

DD 61974/1(8)/3717 100 6/57 R

This invention relates to microbicidal compositions characterized by a high degree of toxicity to bacteria and fungi with which they come into contact and to a process for preparing such compositions. The products are characterized by a low degree of toxicity to the higher animals and by the freedom from discoloration of tissues and other objects with which they come in contact. (The present Application is a Divisional Application from Application Number 25122/54 (Serial No. 25 769, 799) dated August 30th, 1954.)

The treatment of articles, such as those made of fabrics, rubber goods, paper, leather, felt, synthetic organic plastics, ceramics and other substances, to render them lethal over long periods of storage and use to micro organisms coming into contact with them has long presented a problem for which no ready solution free of other undesirable effects has heretofore been found. The problem of controlling the undesirable effects caused by the invasion of bacteria, viruses and fungi of many kinds in the vegetable and animal kingdoms and the difficulties often encountered in killing the invading populations, not only on living plants and animals but also on the many non-living articles which may serve as carriers and harborers for them, are well known. The advantages of compositions which would be

them unsuited for many uses or which render their application difficult. For widespread use such substances should be non-toxic to humans and the higher animals, they should be non-irritating and non-staining when applied to sensitive living or inanimate tissues and, for most applications, they should be devoid of odor and color and should not themselves become colored or develop an odor with the passage of time.

It has long been known that silver salts which furnish at least a minimum concentration of silver ions in aqueous mixtures have strong germicidal properties. Such silver compounds have, however, been utilized to only a very limited extent as germicides because of their known effects in staining tissues and in becoming colored when exposed to light, especially when in contact with proteins. Silver compounds which are highly soluble in water, such as silver nitrate, are unsatisfactory for most such uses because they are removed easily by washing and because of their well known effect in coagulating and precipitating protein. Colloidal silver has, of course, been used for certain limited germicidal purposes but is highly undesirable in applications where the development of color or staining cannot be tolerated.

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International Classification :—A61l. C11d.

COMPLETE SPECIFICATION

Improvements in or relating to Microbicidal Compositions

I, STANLEY DUNLOP, a British Subject, of the firm H. D. Fitzpatrick & Co., 3, Gray's Inn Square, London, W.C.1, England, do hereby declare the invention (as communicated

5 to me by PERMACHEM CORPORATION, a Corporation organised under the laws of the State of Delaware, United States of America, of 5610, Georgia Avenue, West Palm Beach, Florida, United States of America), for which

10 I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to microbicidal compositions characterized by a high degree of toxicity to bacteria and fungi with which they come into contact and to a process for preparing such compositions. The products are characterized by a low degree of toxicity to 15 the higher animals and by the freedom from discoloration of tissues and other objects with which they come in contact. (The present Application is a Divisional Application from Application Number 25122/54 (Serial No. 25 769, 799) dated August 30th, 1954.)

The treatment of articles, such as those made of fabrics, rubber goods, paper, leather, felt, synthetic organic plastics, ceramics and other substances, to render them lethal over 20 long periods of storage and use to micro organisms coming into contact with them has long presented a problem for which no ready solution free of other undesirable effects has heretofore been found. The problem of controlling the undesirable effects caused by the invasion of bacteria, viruses and fungi of many kinds in the vegetable and animal kingdoms and the difficulties often encountered in killing the invading populations, not only on 25 living plants and animals but also on the many non-living articles which may serve as carriers and harborers for them, are well known. The advantages of compositions which would be

effective in killing microorganisms falling on them or which could be applied to surfaces 45 and other places where microorganisms exist and which would effectively destroy the microorganisms are apparent.

Many substances are known which are toxic to bacteria or to fungi, or to both, and many 50 attempts have been made to utilize such substances either alone or combined with other substances to control undesirable microorganisms. Most substances which have heretofore been available have, however, possessed 55 other undesirable properties which render them unsuited for many uses or which render their application difficult. For widespread use such substances should be non-toxic to humans and the higher animals, they should be 60 non-irritating and non-staining when applied to sensitive living or inanimate tissues and, for most applications, they should be devoid of odor and color and should not themselves become colored or develop an odor with the 65 passage of time.

It has long been known that silver salts which furnish at least a minimum concentration of silver ions in aqueous mixtures have strong germicidal properties. Such silver 70 compounds have, however, been utilized to only a very limited extent as germicides because of their known effects in staining tissues and in becoming colored when exposed to light, especially when in contact with proteins. Silver compounds which are highly soluble in water, such as silver nitrate, are unsatisfactory for most such uses because they are removed easily by washing and because of their well known effect in coagulating and precipitating protein. Colloidal silver has, of course, been used for certain limited germicidal purposes but is highly undesirable in applications where the development of color or staining cannot be tolerated.

85 It has now been found that certain of the

sparingly water-soluble silver salts can be utilized readily in the preparation of effective microbicidal compositions. Powders, ointments, soaps, sizing materials and the like 5 can be prepared which exhibit a high degree of fungicidal and bactericidal effectiveness.

The new compositions comprise a sparingly water-soluble germicidal silver compound 10 which is substantially white in colour and which normally becomes discoloured on exposure to light, and a light stabilizer for the silver compound. When a high degree of fungicidal effectiveness is also desired, a sparingly water-soluble salt of a fungicidal organic acid is also included in the composition, the fungicidal salt being selected so that in contact with water it furnishes a fungicidal concentration of the organic acid anions but so 15 that it does not reduce the concentration of silver cations in the aqueous mixture below that necessary to exert the bactericidal effect of the silver cations.

The compositions can be prepared in 20 several ways depending upon the particular product which is desired. In preparing powdered mixtures, ointments, suspensions and lotions, the silver salt and the light stabilizer, together with the fungicidal compound, if 25 desired, can conveniently be milled or agitated with the other ingredients of the mixture to distribute them thoroughly throughout the mixture. In certain cases, especially in the case of powdered substances or suspension of 30 powders one or more of the ingredients normally used in preparing the mixture can serve as part or all of the light stabilizer and in such cases the deliberate addition of another substance for the specific purpose of stabilizing 35 the silver salt against the effect of light can often be omitted.

Thus, a talc preparation can be prepared 40 readily by suspending talc, which acts as the light stabilizer, in water, dissolving silver nitrate in the suspension and subsequently precipitating silver chloride on the talc by adding a solution of sodium chloride to the mixture. After adequate stirring, the mixture is filtered and washed thoroughly with water and dried. 45 It is then broken up and milled with calcium undecylenate to form a highly effective germicidal and fungicidal dusting powder which is remarkably resistant to darkening on exposure to light and which can be used on delicate 50 membranes without irritation or staining of the membrane.

In an alternative procedure for preparing a comparable composition, talc is suspended in water, silver nitrate is added and silver chloride 55 precipitated by the addition of sodium chloride as before and then, without filtering, a desired quantity of ammonium or other soluble undecylenate is added to the mixture and the latter stirred thoroughly. Sufficient calcium chloride is then added to precipitate cal-

cium undecylenate and the mixture filtered, washed and dried as before.

In still another alternative procedure, talc is suspended in water, silver nitrate and ammonium undecylenate are added, together with 70 an excess of ammonia to prevent the precipitation of silver undecylenate. After the addition of sufficient calcium chloride, the mixture is carefully neutralized, e.g., with dilute hydrochloric acid, to precipitate silver chloride and 75 calcium undecylenate and then filtered, washed and dried as before. It is sometimes advisable when following this procedure to filter the mixture while it is still slightly alkaline to insure a more color-stable product. Insofar 80 as has been observed, these three methods for preparing a dusting powder lead to products which are substantially equivalent.

In other instances, the silver salt and the light stabilizer can be prepared as a separate 85 mixture, e.g., by milling together or by co-precipitation from solution, and this mixture then incorporated in the powder, suspension or lotion, to which it is desired to impart microbicidal properties. 90

The composition of the invention is susceptible to considerable variation both as to the proportions of the essential ingredients noted and as to the inclusion of other substances to impart specific properties to the composition. 95 It is advisable from economic considerations to use as low a proportion of the silver compound as possible to obtain the desired bactericidal effect. Generally speaking, from about 0.05 to about 1.0 per cent by weight of 10 silver compound in the composition will be found suitable, although somewhat lower proportions can often be used and higher proportions can, if desired, be employed.

The proportion of fungicidal compound can 10 also be varied over a wide range, depending upon the fungicidal effectiveness of the particular compound employed, the particular organism which it is desired to control, and other factors. In most instances, when a salt 11 of the preferred undecylenic acid is employed, the composition can with advantage contain from about 1.0 to about 10.0 per cent by weight of the fungicidal compound, although lower proportions are often effective. Higher 11 proportions can, of course, be used, if desired. The light stabilizer may constitute a major proportion, i.e., at least about 50 per cent by weight, of the composition.

The composition can also be modified in 12 numerous ways to adapt it for particular uses. Flavoring agents or odorants of various sorts can be included as well as astringents, skin conditioners and the like. It appears that in certain instances the pH of the composition is 12 a contributing factor to its bactericidal or fungicidal effectiveness. Compositions comprising a small proportion of a free basic nitrogen compound such as ammonia, monoethanolamine, triethanolamine and the like, 13

often exhibit a somewhat greater bactericidal effect than similar compositions identical therewith except for the absence of the free basic nitrogen compound. The same effect is also sometimes observed when the composition includes an ammonium salt, such as ammonium carbonate, diammonium phosphate, ammonium sulfate, ammonium chloride and the like. Compositions having a pH too far removed from neutral are likely to be irritating to living tissue and should be avoided when such use is intended. It is thought that the remarkable effectiveness of the composition when applied externally to the skin may to some extent be due to the presence in the perspiration with which it comes in contact of traces of ammonia, ammonium salts or other basic nitrogen compounds. Compositions modified by the addition of tannic acid are also of value as preparations for treating burns.

As has been indicated previously, the composition of the invention is useful for a great many applications for controlling fungicidal, bactericidal and virucidal infections and contaminations both when used topically on living tissue and on inanimate objects. The extent of its usefulness can be judged by its effectiveness *in vitro* in killing or preventing the growth of such representative microorganisms as *Staphylococcus aureus*, *Escherichia coli*, *Clostridium welchii*, *Astridium sporogenes*, *Eberthella typhosus*, *Salmonella paratyphi*, *Proteus mirabilis*, *Shigella dipenteriae*, *Streptococcus hemolyticus*, *Diplococcus pneumoniae*, *Aspergillus niger*, *Penicillium notatum*, *Trichophyton interdigitale*, *Trichophyton gypseum*, *Chaetomium globosum*, *Myrothecium verrucaria*, *Aspergillus terreus*, and the like.

As has been noted previously, one essential ingredient of the composition of the invention is a sparingly water-soluble silver salt. Considerable latitude is possible in the selection of the particular silver salt which can be employed, due consideration being given to the facts that it must furnish a germicidal concentration of silver ions in contact with water or adsorbed moisture but that it must not be sufficiently soluble to be removed easily by washing or to lead to the undesirable effects in the way of discoloration generally encountered when attempting to use a highly water-soluble silver salt, such as the nitrate, as a germicide. The sparingly water-soluble silver salts which can be used are those which have a solubility in water greater than about that of silver sulfide but not appreciably greater than about that of silver sulfate. For most practical purposes, the silver compound selected will be a halide or a phosphate. In most instances silver chloride is preferred because of its advantageous solubility characteristics and because of its ready availability whether used as such or whether prepared during the operation of the process by pre-

cipitation methods. It has also been observed that the halides of silver, particularly the chloride are somewhat less liable in the presence of the light stabilizer to become discolored upon exposure to sunlight than are the phosphates 70 and that when using the phosphate a higher ratio of light stabilizing compound to silver compound is generally desirable than when using silver chloride.

The light stabilizer referred to herein is a 75 substance which absorbs, or is opaque to, light of a wave length which causes discolouration of a sparingly water-soluble silver compound and which, when in aqueous admixture with the compound, does not deplete the silver ions 80 in the mixture to an extent such that the mixture is no longer germicidal. The light stabilizer can be either inorganic or organic in nature, and can be either a liquid, a solid or a paste. Solid light stabilizers should be 85 finely divided and mixed thoroughly with the finely divided silver compound. The finely divided silver compound should be dispersed in the light stabilizer when the latter is a liquid or paste. Examples of inorganic compounds 90 which can be used as light stabilizers include water-insoluble phosphates, sulfates, silicates, and many other simple and complex inorganic salts. Generally speaking, the phosphates of the alkaline earth metals, including magnesium, are preferable from a practical standpoint because of their ready availability, low cost and advantageous solubility and color characteristics. Such substances as alumina, silica, diatomaceous earth, calcium carbonate, 95 zinc oxide and magnesia can also be employed advantageously. It has been found that conventional ointment bases are also suitable as light stabilizers, for example boric acid ointment, zinc oxide ointment and camphor ointment. Soaps derived from a basic nitrogen compound as the base may also be used as light stabilizers. Thus the composition can be formulated as a dry powder, as an ointment or lotion, e.g., toothpastes, dental creams, 100 shaving creams and after shave lotions, and as a germicidal and fungicidal soap.

Of particular interest for certain applications is the use of starch as at least a part of the light stabilizer. Using compositions prepared in this way, fabrics can be starched using conventional starching procedures to impart to them a high degree of resistance to contamination by bacteria and fungi over long periods of time. This effect can, if desired, 115 be obtained by using an amount of starch which does not appreciably stiffen the fabric and the treated fabric retains its resistance to bacterial and fungus infections for long periods of time and even through several washings 120 with hot soap solution, the starch appearing to exert a "binding effect" in addition to its function as a light stabilizer. Such starch-containing compositions are of value in the treatment of clothing, bedding, bandages and many 125 130

other fabric articles. Similar effects can be obtained using a non-starch sizing, such as methyl cellulose, ethyl cellulose, polyvinyl acetate and other suitable plasticized or unplasticized resins, many of which exert an even greater binding effect than starch.

Also of particular interest are bactericidal and fungicidal soaps and detergents prepared in accordance with the invention, particularly those prepared using amine salts, e.g., the alkyloamine salts, such as the monoethanolamine and triethanolamine salts, of fatty acids, such as stearic, oleic and palmitic acids, as a base and light stabilizer. Soaps prepared using these bases, as well as those prepared using many of the synthetic detergents, maintain a high degree of bactericidal and fungicidal activity when dispersed in water. It has been observed that the ordinary conventional alkali metal soaps appear to destroy the bactericidal and fungicidal effectiveness of the composition when included therein and for this reason are not generally considered suitable. Synthetic detergents, such as the amine salts of sulfated fatty alcohols, can be used in preparing the composition, if desired.

It has been mentioned previously that a sparingly water-soluble salt of a fungicidal organic acid can be employed in the process when a composition or article of highly fungicidal effectiveness is desired. The preferred fungicidal organic acids are the saturated and unsaturated aliphatic organic acids having from 3 to 11 carbon atoms in molecule. Such acids include propionic, caproic, caprylic, pelargonic, undecylenic, valeric, sorbic, oleic, and hexenoic acids. In addition to these, however, fungicidal organic acids of other series can be employed, such as benzoic and salicylic acids. Salts of the fungicidal acids which are of particular value are the sparingly soluble aluminium, zinc, magnesium and alkaline earth metal salts. The fungicidal salt should, of course, be chosen with due regard to its toxicity to the higher animals where this is a factor. The fungicidal salt should also furnish, when the composition is in contact with water, a fungicidal concentration of the organic acid anions but should not deplete the aqueous mixture of silver cations to such an extent that the germicidal effectiveness of the latter is impaired. It has been found in practice that the alkaline earth metal salts of undecylenic acid, particularly calcium undecylenate which has not been described previously, can generally be used with advantage.

In the examples which are given below, the products prepared were tested in most instances using a modification of the United States Food & Drug Administration method for assaying penicillin employing an agar medium.

EXAMPLE 1

A first solution was prepared by dissolving 65 10 grams of silver nitrate and 5 grams of crys-

talline magnesium nitrate in 1000 milliliters of water. A second solution was prepared by dissolving 8 grams of sodium chloride, 10 grams of disodium phosphate and 200 milliliters of aqua ammonia in 800 milliliters of water. Two hundred grams of talcum powder was stirred thoroughly for 10 minutes with 400 milliliters of the first solution. Four hundred milliliters of the second solution was then added and the stirring continued for another 15 minutes. The mixture was filtered, the separated powder was washed with water until free of phosphate ions and then air dried over night and subsequently dried in an oven at 70°—90° C. The dry cake was then pulverized. The powder was pure white in color, did not discolor after 10 days exposure to sunlight and was antiseptic and self-sterilizing.

In similar manner, and using solutions similar to those described above, titanium dioxide powder, dental magnesium carbonate and powdered aluminium oxide are rendered antiseptic and self-sterilizing.

EXAMPLE 2

90 A bactericidal powder was prepared by stirring together a mixture of 40 g. of calcium carbonate and a solution of 2 g. of silver fluoride in 200 ml. of water. A solution consisting of 10 g. calcium chloride, 50 ml. aqua ammonia and 150 ml. of water was then added and the mixture stirred for several minutes and then filtered. The precipitate was washed with water and dried at 70°—90° C. It was antiseptic and self-sterilizing. The product contained silver chloride and calcium fluoride as the co-precipitated salts.

EXAMPLE 3

95 A powder containing one per cent by weight of silver chloride was prepared by mixing thoroughly together one part by weight of very finely powdered silver chloride, which had been protected from the light to prevent its discoloration, and 99 parts of talcum powder. A sample of the dry mixture thus prepared was 100 exposed to direct sunlight in the open air for about 8 weeks. No darkening of the sample occurred. A sample of the silver chloride used in preparing the mixture when exposed to light under comparable conditions was practically black at the end of the exposure period.

110 Mixtures were prepared in a similar manner containing 0.1, 0.2, 0.5 and 2.0 per cent by weight of silver chloride and exposed to light in the same manner as the one per cent mixture. At the end of the test period the mixtures containing 0.1, 0.2 and 0.5 per cent of silver chloride had not darkened and the mixture containing 2.0 per cent of silver chloride showed only a very slight grayish discoloration. Similar mixtures containing 5 to 10 per cent of silver chloride darken rapidly when exposed under comparable conditions.

EXAMPLE 4.

A mixture containing 44 grams of talcum powder, 1 gram of silver chloride and 5 grams calcium undecylenate was prepared by mixing 5 the dry powdered substances together until a uniform product was obtained. The mixture contained 2 per cent silver chloride, 10 per cent calcium undecylenate and 88 per cent talcum. It did not discolor when exposed to 10 direct sunlight for several weeks.

The powdered product obtained was tested for antiseptic properties by spreading a few tenths of a gram of the powder in a small depression formed on the surface of an inoculated agar plate and incubating the plate under conditions favoring the growth of the organism. When the organism used was *Staphylococcus aureus* the clear zone of inhibition around the powder was 2.0 to 2.2 millimeters wide. When the test organism was *Escherichia coli* the clear zone of inhibition around the powder was 3.0 to 3.2 millimeters wide. When the organism employed was the fungus *Trichophyton gypseum* the clear zone 20 of inhibition around the powder was 10.0 to 25 10.5 millimeters wide.

EXAMPLE 5.

Five grams of finely powdered calcium undecylenate was mixed thoroughly with 26.4 30 grams of talcum powder and the mixture blended thoroughly with an intimate mixture of 0.6 gram of silver chloride in 43 grams of talcum powder. The resulting mixture was then mixed thoroughly with 25 grams of 35 powdered corn starch. The final product contained 0.6 per cent by weight of silver chloride, 5 per cent of calcium undecylenate and 25 per cent of starch and was not discolored by several weeks exposure to direct sunlight.

EXAMPLE 6.

Forty-one hundredths gram of sodium chloride is dissolved in about 300 milliliters of water and the solution heated at about 80° C. Ninety-nine grams of talcum powder is then 45 added with vigorous agitation followed by a solution of 1.18 grams of silver nitrate in 100 milliliters of water. The mixture is stirred for a few minutes, filtered and the cake washed substantially free of soluble chlorides or silver 50 salts with hot water. The washed product is then dried *in vacuo*. The product thus obtained is a white powder containing one per cent of silver chloride and is not discolored by several weeks exposure to light.

EXAMPLE 7.

Ten grams of a microbicidal starch prepared according to the procedure of Example 5 was stirred into a paste with 25 to 30 milliliters of cold water. The paste was then stirred slowly 60 into sufficient hot water (about 80° C.) to make one liter of finished product. Vigorous agitation of the mixture was continued for

about 10 minutes and the dispersion then allowed to cool almost to ordinary room temperature. Pieces of cotton fabric were then 65 dipped in the starch dispersion and air dried. After drying, the fabrics were ironed. The ironed fabric was bactericidal, fungicidal and self-sterilizing.

EXAMPLE 8.

Nine grams of lanolin and 20 grams of petrolatum were melted on a water bath and mixed thoroughly. Five grams of calcium undecylenate and one gram of silver chloride 70 were ground together in a mortar and the fine 75 powder stirred thoroughly into the mixture of lanolin and petrolatum. Twenty millimeters of water were added and the stirring continued until the mixture had thickened to a stiff 80 ointment. The resulting ointment was bactericidal when tested against *Staphylococcus aureus*, *Escherichia coli* and fungicidal when tested against *Trichophyton gypseum*.

EXAMPLE 9.

Fifteen grams of Carbowax 1000 (manufactured by Carbide and Carbon Chemicals Company of America) was dissolved in 20 milliliters of hot distilled water. Two and one-half milliliters of an aqueous one per cent solution of silver undecylenate containing 90 sufficient monoethanolamine to dissolve the silver undecylenate was then added to the Carbowax solution, followed by one gram of undecylenic acid saponified with 2.5 grams of monoethanolamine dissolved in 9 milliliters of 95 distilled water. The lotion was thoroughly stirred and cooled to ordinary room temperature. The finished lotion contained 0.05 per cent silver undecylenate, 2 per cent monoethanolamine undecylenate, 5.35 per cent free 100 monoethanolamine, 30 per cent Carbowax and 62.6 per cent distilled water. The finished lotion was both bactericidal and fungicidal.

EXAMPLE 10.

Fifteen grams of calcium undecylenate, 3 105 grams of silver chloride and 282 grams of U.S.P. calcium carbonate, all in finally divided form, were mixed thoroughly together and a few drops of peppermint oil was blended into the mixture. The resulting mixture was a 110 satisfactory tooth powder having both bactericidal and fungicidal properties when tested as previously described.

EXAMPLE 11.

A monoethanolamine soap was prepared by 115 mixing 100 grams of technical oleic acid with 200 milliliters of monoethanolamine. The soap was dissolved in 1 liter of distilled water in which it was completely soluble. A portion of the solution was set aside and labeled "C" for 120 use as a control.

Six-tenths gram of silver chloride was dissolved in 10 milliliters of monoethanolamine and the solution mixed thoroughly with

another 600 milliliter portion of the soap solution at ordinary temperature. This solution was labeled "A".

Three grams of undecylenic acid were dissolved in 10 milliliters of monoethanolamine and added to yet another 300 milliliter portion of the soap solution at ordinary temperature. This solution was labeled "B".

A number of cotton swatches were contaminated by dipping for 15 seconds in an aqueous dispersion of *Staphylococcus aureus* and *Escherichia coli*. Some of the contaminated swatches were then immersed at ordinary temperature for 15 minutes in a 1:5 dilution with water of solution "A", others were dipped under the same conditions in solution "B" and still others in solution "C". The procedure was then repeated using other contaminated swatches and a 1:10 dilution of solutions "A", "B" and "C". The swatches were then rinsed thoroughly in water and each incubated on an agar plate at 37° C. for 24 hours. No growths of the organisms were detected on the plates containing swatches which had been dipped in either of the dilutions of solutions "A" and "B". All contaminated swatches which had been dipped in the control solution "C" were overgrown with both of the organisms.

The above procedure was repeated using a water suspension of spores of *Trichophyton gypseum* as the contaminating organism and using a 1:10 dilution of each of the three solutions "A", "B" and "C". The rinsed swatches were incubated on plates of Sabouraud's agar at ordinary room temperature for 10 days. At the end of this period swatches which had been dipped in the control solution "C" were badly overgrown with fungus whereas the swatches dipped in solution "B" and "C" showed no fungus growth whatsoever.

Soap solutions comparable to those described above, but using an ordinary laundry soap in place of the monoethanolamine soap, gave no control of the growth of contaminating organisms in tests carried out in a manner similar to those described above.

What I claim is:—

50 1. A microbicidal composition comprising a

finely divided sparingly water-soluble silver compound, which is substantially white in colour and which normally becomes discoloured on exposure to light, and intermingled intimately therewith as a light stabilizer therefor, a substance opaque to light of a wave length causing discolouration of the silver compound, the composition when in aqueous admixture furnishing a germicidal concentration of silver ions.

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2. A composition as claimed in Claim 1, and additionally containing a sparingly water-soluble fungicidal compound of a fungicidal organic acid.

3. A composition as claimed in Claim 1 or 65 2, wherein the silver compound is a silver halide or phosphate.

4. A composition as claimed in Claim 3, wherein the silver halide is silver chloride.

5. A composition as claimed in Claim 2, 3 70 or 4, wherein the fungicidal compound is a salt of an aliphatic acid having from 3 to 11 carbon atoms in the molecule.

6. A composition as claimed in Claim 5, wherein the fungicidal compound is calcium 75 undecylenate.

7. A composition as claimed in any of Claims 1 to 6, wherein the light stabilizer is a sparingly soluble or substantially insoluble material.

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8. A composition as claimed in any preceding claim, wherein the light stabilizer is the major proportion of the composition.

9. A composition as claimed in Claim 8, wherein, at least, the major proportion of the 85 light stabilizer is starch.

10. A composition as claimed in Claim 8, wherein the light stabilizer is an ointment or lotion base.

11. A composition as claimed in Claim 8, 90 wherein the light stabilizer is a basic nitrogen soap base.

12. A microbicidal composition substantially as hereinbefore described with reference to any of the specific examples.

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